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(54) Title: DRILLING FLUID

(57) Abstract

A water-based drilling fluid (WBM) comprises as additive one or more alcohol ethoxylates in which the alcohol chain has at least 5 carbon atoms. The number of carbon atoms in the alcohol is preferably in the range 5 to 14, more preferably 6 to 10, and the alcohol is preferably straight chain. The number of ethylene oxide units is preferably in the range 5 to 20, more preferably 6 to 12. Two typical additive molecules suitable for use in the drilling fluid of the invention are: $C_6H_{13}O(C_2H_5O)_7H$ and $C_8H_{17}O(C_2H_5O)_7H$. Drilling fluids in accordance with the invention have been found in laboratory tests to exhibit improved shale inhibition properties as compared with known polyol containing WBM, particularly in the absence of added potassium ions. This is environmentally advantageous.

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Drilling Fluid

This invention concerns drilling fluids, particularly water-based drilling fluids.

Background to the Invention

Drilling fluids are used in well drilling operations, eg during drilling of oil and gas wells. During drilling, drilling fluid is pumped down a drillstring, discharged through ports in the drill bit and returned to the surface via the annulus between the drillpipe and the surrounding formation. The drilling fluid performs a variety of functions including cooling and lubricating the drill bit and drillstring, removing rock cuttings generated during the drilling process and carrying them to the surface, suspending cuttings in the annulus when pumping stops, preventing squeezing in or caving of the formation and keeping formation fluids at bay.

Drilling fluids generally comprise a carrier, a weighting agent and chemical addititives. Drilling fluids fall into two main categories: water-based drilling fluids, also known as water based muds (WBM), in which the carrier is an aqueous medium; and oil-based drilling fluids, also known as oil-based muds (OBM), in which the carrier is oil. OBM are technically superior to WBM in certain important respects, including the comparative lack of adverse reactivity of OBM with shales, one of the most commonly encountered rock types during drilling for oil and gas. Use of OBM, however, has the disadvantage of resulting in production of large quantities of oil-contaminated waste products such as cuttings that are difficult to dispose of in an environmentally acceptable way. While use of WBM is environmentally more acceptable than OBM, the performance of WBM, particularly when drilling through water sensitive rocks such as shales, is technically inferior to that of OBM. Shales exhibit great affinity for water, and adsorption of water by shales causes the shale to swell and produces chemical changes in the rock which produce stresses that weaken the formation, possibly leading to erosion of the borehole or loss of structure. This can lead to drilling problems such as stuck pipe. In addition inferior wellbore quality may hinder logging and completion operations.

Much effort has been put into improving the performance of WBM relative to shales, namely improving the level of so called shale inhibition of WBM. Various chemical additives have been incorporated in WBM in attempts to improve shale inhibition. In particular water soluble glycols or polyols (ie. molecules containing more than one hydroxyl groups) are widely used for this purpose, typically being added to WBM in amounts in the range 3 to 10% by weight. Polyols used in this way include, for example, glycerols, polyglycerols, glycols, polyalkylene glycols (PAG), eg polyethylene glycols

(PEG), polypropylene glycols (PPG) and copolymers of ethylene and propylene glycols, alcohol ethoxylates (AET) and glycol ethers. A typical inhibitive AET is an n-butanol derivative of ethylene oxide. The PAGs can have a range of ethylene oxide: propylene oxide (EO:PO) ratios and can be random or block copolymers; a frequently used material of this type is understood to be a random copolymer with an EO:PO ratio of about 1:1. See, for example EP 0495579, US 4830765, US 4172800. For further discussion of this subject see, for instance, The Society of Petroleum Engineers Reports SPE 25989 (Reduced Environment Impact and Improved Drilling Performance With Water-Based Muds Containing Glycols) and SPE 28818 (Water Based Glycol Drilling Muds - Shale Inhibition Mechanisms) and also Schlumberger Oilfield Review, April 1994, pages 33 to 43 (Designing and Managing Drilling Fluid).

The shale inhibition properties of polyol-containing WBM can be enhanced by incorporation of potassium salts, eg potassium chloride, possibly in combination with gypsum. However, the shale inhibition properties of even the best known potassium and polyol-containing WBM are much inferior to those of OBM. Further, the use of potassium can present waste disposal problems, as there are certain regions, eg. The Gulf of Mexico, where the discharge of potassium to the environment is prohibited or severely restricted. In addition, the use of potassium-containing WBM can present problems in land drilling where the contamination of ground water by potassium-containing drilling waste is considered unacceptable.

It has now been found that the shale inhibition properties of WBM can be improved by use of novel polyol additives in the form of various alcohol ethoxylates.

Summary of the Invention

According to the present invention there is provided a water-based drilling fluid comprising as additive one or more alcohol ethoxylates in which the alcohol chain has at least 5 carbon groups.

While it is known to use alcohol ethoxylates (AETs) with short alcohol chains, up to C_4, as additives for WBM, the use of AETs with longer alcohol chains has not hitherto been proposed for this purpose.

AETs have the general formula $C_nH_{2n+1}O(C_2H_5O)_mH$. In accordance with the invention $n \geq 5$. The alcohol can be straight or branched chain. n is preferably in the range 5 to 14, more preferably 6 to 10. For higher values of n there is a tendency for the ethoxylate to exhibit surfactant properties with undesirable frothing and foaming, but this is reduced by use of branched chain alcohols. It is thus preferred to use shorter (n=6 to 10) straight chain alcohols.

n is preferably even as molecules with odd valves of n tend to be more expensive.

The number of ethylene oxide (EO) units, ie. the valve of m, is not critical. It is preferred that this is not too high so that the molecular weight of the molecule (and viscosity of the chemical) is not too high. m is preferably in the range 5 to 20, more preferably 6 to 12.

Mixtures of ethoxylates may be used.

The additive molecules preferably generally have molecular weights of greater than about 400 and less than about 3000, and have substantial solubility in distilled water, seawater and potassium brines at ambient temperatures.

Additives for use in the invention are either commercially available, eg from Dowell Schlumberger, or can be readily synthesised.

The additives are typically used in WBM in amounts in the range 3 to 10% by weight, preferably 3 to 5% by weight.

The drilling fluid of the invention may otherwise be of conventional formulation, with the aqueous medium typically comprising fresh water, salt water, other salt solutions or mixtures thereof.

Other additives may be included in the drilling fluid in conventional manner. In particular, potassium ions, eg from potassium chloride, may be included to improve shale inhibition properties.

Drilling fluids in accordance with the invention have been found in laboratory tests to exhibit improved shale inhibition properties as compared with known polyol containing WBM, particularly in the absence of added potassium ions. This is environmentally advantageous, as discussed above.

The mechanisms of shale inhibition is not at present understood, but it is thought (without wishing to be bound by theory) that the improved shale inhibition properties obtained with the drilling fluids of the invention result from enhanced hydrophobic interaction between adjacent polyol molecules adsorbed on clay surfaces of shales due to the increased hydrophobicity of the polyol resulting from the presence of a longer alcohol chain in the ethoxylate than is conventional.

The invention will be further described, by way of illustration, in the following Example.

Example

The level of shale inhibition provided by different drilling fluid additives and formulations is routinely assessed by a number of laboratory techniques. Tests such as cuttings dispersion and shale swelling are suitable for the rapid screening of new additives and are widely use in the industry. A good indication of the inhibitive properties of an additive can also be obtained by immersing clay films made from montmorillonite/water pastes in the test fluid and noting whether the film disperses, softens or remains intact. This approach is particularly suitable for screening low viscosity, water-soluble species such as polyols and the results correlate qualitatively with cuttings dispersion data.

The film immersion technique was used to compare the inhibitive properties of three ethoxylates (two within the scope of this invention and one not) with 3 established polyol inhibitors. All tests were carried out using solutions containing 5 wt % polyol. Two tests were carried out on each polyol: one using distilled water solutions and one using polyol dissolved in a 7% aqueous solution of potassium chloride. The films were immersed in the fluid for 16 hours before being recovered and their condition assessed visually.

The results of these tests are given in Table 1. The three conventional polyols used for comparison were polyethylene glycol (PEG), polyalkylene glycol (PAG) and an n-butanol ethoxylate (BET). The average molecular weights of these materials were approximately 600, 650 and 320, respectively. The PAG was a random copolymer of ethylene (EO) and propylene oxide (PO) with an EO:PO ratio of approximately 1:1. The ethoxylates used all comprised approximately 7 EO units (ie m = 7) and linear alcohols of 4, 6 and 8 carbon atoms (ie n = 4, 6 and 8) for M1, M2 and M3, respectively. M1 is thus chemically similar to BET and is outside the scope of the invention.

TABLE 1

TEST FLUID	CONDITION OF CLAY FILM AFTER EXPOSURE TO TEST FLUID
5% PEG	Swollen and dispersed
5% PEG/7% KCl	Firm and intact
5% BET	Swollen and dispersed
5% BET/7% KCl	Firm and intact
5% PAG	Soft but intact
5% PAG/7% KCl	Firm and intact
5% M1	Swollen and dispersed
5% M1/7% KCl	Firm and intact
5% M2	Soft-to-firm and intact
5% M2/7% KCl	Firm and intact
5% M3	Firm and intact
5% M3/7% KCl	Firm and intact

The results show that, in the distilled water environment, higher levels of inhibition can be obtained with the M2 and M3 ethoxylates of the invention than with the M1 ethoxylate and the conventional PEG, PAG and BET additives.

CLAIMS

1. A water-based drilling fluid comprising as additive one or more alcohol ethoxylates in which the alcohol chain has at least 5 carbon groups.

2. A drilling fluid according to claim 1, wherein the ethoxylate comprises alcohol with a chain length in the range C_5 to C_{14}.

3. A drilling fluid according to claim 2, wherein the ethoxylate comprises alcohol with a chain length in the range C_6 to C_{10}.

4. A drilling fluid according to claim 1, 2 or 3, wherein the ethoxylate comprises straight chain alcohol.

5. A drilling fluid according to any one of the preceding claims, wherein the ethoxylate has between 5 and 20 ethylene oxide (EO) units.

6. A drilling fluid according to claim 5, wherein the ethoxylate has between 6 and 12 EO units.

7. A drilling fluid accoding to any one of the preceding claims, wherein the ethoxylate comprises $C_6H_{13}O(C_2H_5O)_7H$ and/or $C_8H_{17}O(C_2H_5O)_7H$.

8. A drilling fluid according to any one of the preceding claims, wherein the additive comprises molecules having molecular weights of greater than about 400 and less than about 3000 and having substantial solubility in distilled water, seawater and potassium brines at ambient temperatures.

9. A drilling fluid according to any one of the preceding claims, wherein the additive is present in an amount in the range 3 to 10% by weight.

10. A drilling fluid according to claim 9, wherein the additive is present in an amount in the range 3 to 5% by weight.

11. A drilling fluid according to any one of the preceding claims, comprising aqueous medium of fresh water, salt water, other salt solutions or mixtures thereof.

12. A drilling fluid according to any one of the preceding claims, comprising one or more further additives.

13. A drilling fluid according to claim 12, comprising potassium salt additive.

14. A drilling fluid according to claim 13, wherein the potassium salt comprises potassium chloride.

15. A drilling fluid according to claim 1, substantially as herein described.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09K7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,43 02 462 (HENKEL) 30 June 1994 see page 3, line 42 - line 63 see page 5, line 23 - line 60 see page 6, line 24 - line 42 see page 7, line 3 - line 11 see page 7, line 29 - line 43; claims 1,5,15,16	1-6,9-15
Y	US,A,3 396 105 (R.F.BURDYN) 6 August 1968 see column 3, line 51 - column 4, line 27 see column 10, line 57 - column 11, line 8	1-7, 11-15
Y	DE,A,10 52 332 (SOCONY MOBILOIL COMP.) 12 March 1959 see column 2, line 51 - column 3, line 54 see column 5, line 25 - line 48; claims 1-5	1-7, 11-15

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE-A-4302462	30-06-94	AU-B-	5813494	19-07-94
		CA-A-	2152778	07-07-94
		WO-A-	9414918	07-07-94
		EP-A-	0675937	11-10-95
		NO-A-	951618	27-04-95
US-A-3396105	06-08-68	NONE		
DE-A-1052332		NONE		